

unaltered, we raise the value of ψ_1/ψ_2 by 50 per cent., so the question of the compressibility of the material is not unimportant. The above result agrees with Sir Joseph Larmor's (p. 14, *supra*) and with that obtained by combining Terazawa's equations (6) and (7).*

I was not aware of the existence of Sir G. H. Darwin's paper until long after my paper was published, and did not notice the reference in it to Lord Kelvin until the publication of Terazawa's paper led me to restudy the problem.

Experiments on Tribo-Electricity. I.—The Tribo-Electric Series.

By P. E. SHAW, B.A., D.Sc., University College, Nottingham.

(Communicated by Prof. E. H. Barton, F.R.S. Received May 24, 1917.)

CONTENTS.

	PAGE.
I. Historical	16
II. Various Short Tribo-Electric Series	18
III. Apparatus and Methods.....	21
IV. The Full Tribo-Electric Series	23
V. Theory	27
VI. Conclusion	31
VII. Summary	32
List of References	33

The term "Tribo-electricity" is used in O. D. Chwolson's 'Traité de Physique' (1). This term is a convenient equivalent for frictional electricity ($\tau\rho\beta\dot{\gamma}$ = a rubbing).

I.—*Historical.*

Little exact knowledge of tribo-electricity has yet been accumulated, and this subject has certainly not been raised to the dignity of a quantitative science. In the present paper will be found an account of experiments in which the conditions of the solid bodies rubbed together have been greatly varied. Thus, temperature has been changed both before and during friction; the surfaces used have been rubbed with considerable pressure while hot; they have, wherever possible, been rubbed together when flexed; and they have been prepared before rubbing by being ground and polished in various ways. Much information has thus come to light as to the electrical surface conditions of a variety of solids.

* 'Phil. Trans.,' A, vol. 217, p. 37.

Before setting forth the methods and results of this paper, let us note the information previously available. Good summaries of the subject will be found in Wiedemann's 'Electricität' (2) and Chwolson's treatise (1).

The data on the subject altogether lack coherency. The electrical effects obtained by friction had been so often found to be irregular—an irregularity which in great part I explain in this paper—that the subject was in general avoided. One obvious source of uncertainty of action is that rubbing necessarily affects, perhaps destroys, the surfaces under investigation, so that friction, especially if violent, may, in effect, give rise to surfaces of a new kind.

As to recent research on the subject, Héséhous (3), in the opening years of this century (1901–5), brought to light in a series of papers, some new phenomena, and made an attempt to reduce the known facts to some sort of order. He suggested certain generalisations as follows: (1) a polished surface is always + to a matt surface of the same material; (2) a more dense surface is always + to a less dense one of the same material; (3) dust proceeding from a body is always — to the solid substance it leaves. He also made investigations of the action of radium, and he found some materials, *e.g.*, glass, are made more +-forming, whereas others, *e.g.*, ebonite, are made more --forming by the discharge. Further, Héséhous attempted to bring tribo-electric phenomena within the scope of the electron theory. He supposed that electrons pass from the more dense to the less dense of any two bodies brought into contact, this movement of the electrons being facilitated by the change, due to contact, in the surface tension of both bodies at the point of contact. Of the above generalisations, the first and second are shown below to be incorrect; the others have not been directly put to the test.

A few years ago some quantitative researches (perhaps the first ever made on tribo-electricity) came from Bangor, North Wales: from Morris-Owen in 1909 (4), and from W. Morris-Jones in 1915 (5). The apparatus used in the two cases was of the same type. It was arranged that not only the charge (Q) produced, but also the work (W) done in producing it, and the pressure (P) applied in the friction between the solids rubbed, could be actually measured throughout an experiment. Simple relations were found connecting Q, W, and P.

In 1915 I investigated the anomalous effects obtained from glass after heating (6). It was found that glass, which is + to silk, becomes temporarily — to it after being raised to sufficiently high temperature. Further, this anomalous effect was found in a great number of other solids, including metals and ebonite, if rubbed with suitable materials. The general conclusion was reached that this behaviour, after heating, is common to all solids.

The last-named research was the starting part of the present experiments. Its methods have been developed and its conclusions confirmed, while the range of enquiry has been extended to several physical changes other than thermal.

II.—*Various Short Tribo-electric Series.*

In the early pages of most books on electricity is found a series of solid materials arranged in order in such wise that any one of the materials becomes + if rubbed with any other lower down in the series. The arrangement of materials by different authorities ranging over the last 150 years may be here contrasted. In the last list I take from my Table (p. 32) only such materials as are mentioned in the other lists.

Wilcke (1759).	Faraday (1840).	Jamin and Bouthy's 'Physique' (1891).	Shaw (1917).
Glass	Cat's fur	Cat's fur	Glass.
Wool	Wool	Glass	Wool.
Quills	Quills	Wool	Cat's fur.
Wood	Flint glass	Feathers	Pb.
Paper	Cotton	Wood	Silk.
Ground glass	Linen	Paper	Paper.
Pb	Silk	Silk	Cotton.
Sulphur	Hand	Resin	Wood, Fe.
Metals	Wood	Ground glass	Ground glass.
	Fe, Cu, Ag, Pb.		Resin.
	Sulphur		Cu, Ag.
			Sulphur.

If lines were drawn joining like materials in the different lists, there would be many intersections of these lines, showing how differently the solids are arranged. The many disagreements thus displayed show how necessary it is to standardise the materials used. As will be shown in the sequel, it is probable that these dissimilarities arise from the use of different methods or of different materials, or of materials whose surfaces differ in physical condition, rather than from personal errors of observation. This kind of research may seem easy: it is easy to get some results of sorts, but it requires considerable practice and special knowledge of surface conditions to obtain results which will stand repeated tests. The series which I give in the Table (p. 32) is the last of some dozen or so of lists drawn up during many months. At first, errors were made through the employment of faulty methods or from ignorance of the many factors involved. It took considerable time, as one's skill increased, to sort out the materials into their correct places. When the series was considered correct, I prepared a

complete new set of surfaces, and checked the series by going over the whole ground again with these fresh materials.

My complete series is shown in the Table (p. 32). This includes only fairly common solids and one liquid, mercury (whose peculiar action is described later, p. 25).

It is desirable to have a long list, such as this, which contains about seventy-eight materials, for, by including many materials, we obtain more steps from extreme + at the top to extreme — at the bottom. If the steps are many, the gradations will in general be less, and thus smaller differences between substances can be detected than would be possible if only a few steps occur, as in Wilcke's list of nine materials.

In the present section we need only notice column 2, which shows the materials used in normal order. These are in all cases the ordinary commercial article, but, in order to establish standard materials for future reference, particulars will be given in some cases.

Furs.—In rabbit's fur the hairs are clipped short, in imitation of ermine. In opossum's and cat's fur the hairs are of natural length. These furs have been selected from a great number, as giving convenient steps between places 1 and 12 in the Table.

Vitreous Silica, Quartz, and the Glasses.—In places 3 to 9 are shown no less than seven specimens of this family. The quartz is the natural material to which has been given an artificially polished surface. The vitreous silica used has surface smooth from fusion. Three glass surfaces, including glazed porcelain, are smooth from fusion; one is artificially polished, and one surface (place 9) is the edge of thick plate glass, obtained after the plate has been cut by diamond and broken in the usual way.

Wool, Silk, Cotton.—Care must be taken in using fabrics purporting to be made of these materials, especially in the case of silk, which is so often adulterated with other yarn. The standard materials in which I trusted are skeins of yarn. The silk and wool came from yarn merchants, guaranteed pure. The silk has the natural gum washed quite free from it. The cotton used is pure white cotton-wool.

Mica, Calcite.—The natural surfaces of fresh specimens are used after recent cleavage. The surfaces of salt crystals are scraped before use.

Metals and Alloys.—Twenty-three materials are quoted. Their surfaces are used scraped or rubbed with sand-paper, or, where possible, burnished. It is important to avoid surface oxide, sulphide, etc., but no differences have been detected in any metal surface on account of the above different methods of cleaning.

Felt (mixture of hair and wool and other fibres).—The specimens are of

close texture, about 5 mm. thick. The material is such as is used for carpeting.

Vulcanised Fibre.—This red composite material is supplied rolled in sheets and tubes. A tube is polished by rotation in the lathe under the pressure of another tube of the material. No liquid or other foreign material is used in the process.

Woods.—Ebony is the only wood of many tested, which does not occupy place 19. The specimens are planed up smooth and parallel to the grain.

Shellac, Sealing Wax, Resin, Sulphur, are melted and allowed to solidify on glass tubes. The two former must not be raised far above the melting point in the process. This care is necessary to avoid disintegration.

Ebonite.—The solid rod is polished in the same way as vulcanised fibre.

Carbon.—Gas carbon rods, as used for arc lights, and charcoal of various kinds have all the same place (29) in the Table.

Celluloid.—This also is best in its purest form in limpid sheet highly polished. The opaque, less pure, form is higher, about place 29.

Indiarubber.—Under this head is implied the pure, translucent, very elastic, sheet rubber used for mending the inner tube of bicycles. There are many forms of impure rubber; for instance, white rubber is much higher in the Table (place 29).

It is noteworthy that differences of behaviour are easily observable between insulating materials all of one class. In order to indicate how differences in the surfaces not detectable by any other means are easily shown by tribo-electric effects, take a few cases:—

(a) A highly insulating material, such as celluloid or mica sheet, being cut into two pieces, it will generally be found that one piece will be + and the other — when rubbed together. There is nothing whatever in their appearance to show that these pieces cut from the same sheet are in any way different.

(b) Nine different furs tested were found to take definite positions between places 1 and 13 in the Table, various hard siliceous materials falling into place between them as shown.

Furs.	Woods.
(Asbestos.)	Black wolf.
Rabbit.	Caracule.
Fox.	(Vitreous silica.)
(Glass.)	(Glass.)
Opossum.	Astrachan.
Mink.	Cat's skin.
Skunk.	
	(Matt mica.)
	Red deal.
	Canary.
	Box.
	White deal.
	Rosewood.
	Oak.
	Beech.
	Jarra.
	Walnut.
	Mahogany.
	Lignum vitæ.
	(Matt glass.)
	Ebony.

(c) Of 12 different woods, all except one (ebony) form one group, place 19, yet when rubbed together they can be arranged in definite sequence like furs. The lists of furs and wood are given on p. 20.

III.—*Apparatus and Methods.*

The confusion which has been a feature of this subject in the past may be attributed to the uncertainty as to materials used, their past treatment, and the methods employed in experimenting on them. With the attempt to standardise the methods, or at least to specify my own processes, I will give particulars throughout, even though these are admittedly simple.

The materials used may be divided into conductors and insulators. The latter can, in general, be used unmounted; the former (including partial conductors, *e.g.*, wood, cotton fabric, asbestos) must be mounted on a non-conductor. In general, those rods, tubes, or sheets, which have to be mounted are attached by sealing-wax to the inside or outside of glass tubes. It is necessary to have sufficient distance, say 10 cm., between the hand and any conductor undergoing test, for if the hand be nearer it may remove, by induction, any free charge on the material. Easily fused materials, *e.g.*, shellac and paraffin wax, are mounted in a solid lump at the end of a glass tube. Lumps of material, such as minerals or carbon, are held in a clip specially made of ebonite. Mercury is used in a cylinder into which any material can be plunged.

The gold-leaf electroscope used is provided with a shallow horizontal cylinder open at both ends. For charging the electroscope a wire is arranged close to the cylinder. This wire is connected with a live wire of an electric light circuit at 205 volts. As a means of discharging the surfaces, a small bunsen flame is kept alight in front of the observer. The flame itself should never be used as a discharging agent, since most surfaces become abnormal very quickly in the flame. Round the flame is a zone, the discharge zone of air, so highly ionised that any charged body moved about at, say, 10 cm. from the flame for a few seconds becomes completely discharged. The gases rising from the flame are more highly ionised than the air at its side, but there is great danger, if the body be plunged in these gases, that the temperature of the body will rise so far that it will become abnormal.

In investigating critical temperatures (column 4 in Table, p. 32), the substance is heated by being placed on the upper shelf of a copper oven, the oven being swaddled in sheet asbestos. The door of the oven is closed and the temperature is raised by bunsen burners underneath, and is recorded by a thermometer inserted through the top of the oven. It is easy to raise

the temperature slowly to, say, 320° C., which is high enough for present purposes.

As to the condition of the surfaces used, cleanliness is desirable, though apart from chemical impurity, *e.g.*, oxides, sulphides, on metals, dirt does not influence results as much as might be supposed. It is clear that if, for instance, there is a layer of dust on an ebonite rod, this, when rubbed with silk or paper, will be brushed away at the first stroke, and the true surfaces will be brought into contact. But metals must be used free of corrosion by the application of sand paper or by the process of filing or scraping. Apart from metals, it is well to keep such materials as ebonite, gutta-percha, and vulcanised fibre clean by frequent scraping.

It is important to observe that materials, *e.g.*, mica, glass, or celluloid, supposed to be polished are really used in this state. Polished celluloid and ebonite are easily rendered matt at the place of rubbing when pressed on some hard surfaces.

We must observe a uniform method of rubbing the surfaces. Consider, as an example, the case of quartz-silk. If the silk be brushed over the quartz it becomes +, but if rubbed hard on it its charge becomes -. These effects will generally be found when hard surfaces are rubbed with flexible ones, such as fabrics and furs. To take another instance; if a mica sheet be beaten on a glass tube it becomes slightly +, but if rubbed on it strongly -. The latter is the standard way, which I always use, hence in the above examples we place quartz above silk and mica below glass in the Table. Furs themselves are somewhat uncertain. The same specimen of opossum fur may at one end be + to vitreous silica, and at the other be - to it. In such cases as this the experimenter must learn the peculiarities, if any, of the materials he uses.

As will appear later the surfaces of most materials are susceptible of several states, all more or less stable. Thus, if a smooth glass rod be under test it may have its position in the Table at place 3, 5, 8, or 26. But repeated rubbing, gentle heating, and the slow changes which occur with lapse of time will bring the glass to a definite position, say place 5, which is taken to be the position of glass in its most stable state.

It might be thought desirable to use special devices to clear of adsorbed layers the surfaces about to be rubbed. For instance, well-known methods could be suggested, such as (1) tearing off the surface by gelatine films, or (2) scraping *in vacuo*. These processes have been found necessary in other surface experiments, such as surface tension and photo-electricity. But there is an essential difference between the delicate forces at work in the latter subjects and the rough impact of solid on solid, such as occurs in

tribo-electric experiments. In this case, the true surfaces would bear on one another. The actual bearing surface of one solid on another would be so small that the pressure per square millimetre would be enormous, and would suffice to break through any thin outer foreign film, especially one of a liquid condition.

IV.—*The Full Tribo-electric Series.*

At the end of this paper is a Table which gives in compact form the experimental results of this investigation. In the second column are shown the materials used, arranged in 36 standard places. Those in capital type I have found more useful than the rest. The metals are italicised. The whole list from Asbestos at the + end to Indiarubber at the — end may be likened to a staircase of 36 steps, which steps are, of course, unequal in depth to an unknown degree. The list itself could be expanded apparently without limit. Group B follows Group A without break.

Column 3 contains such materials, bright when in column 2, as can be rendered matt by some abrasive, *e.g.* sand paper. It will be observed what a vast disparity there is, in some cases, between the surfaces of the same material when polished and when matt. Thus, the members of the glass family, normally round about place 5, are, when matt, at place 20.

In column 4 are the places of the materials when these have had their surfaces raised above the critical temperature, which temperature where it has been found is inserted in brackets. I call a surface abnormal when, as a result of being heated above a certain temperature, it moves from its normal place in column 2 to some other place in column 4. This particular temperature I call the Critical Temperature (C.T.). There are two ways of making a surface abnormal: (1) By raising the substance as a whole to the C.T. in the air-bath; (2) by passing the surface rapidly through the hot body of a flame. In the latter case (which, of course, is not applicable to all materials), though the interior of the substance may remain cool, the surface particles will be raised to the C.T. in a few seconds or less. Experience shows that the abnormal place of a body in column 4 is always the same by whichever of the above processes this condition is obtained. Suppose a body has been raised to the C.T., and on being rubbed at that temperature is found to be abnormal at place 26. It will remain abnormal when cold and still occupy place 26 in the Table.

It will be observed that the critical temperatures range from 300° for quartz (a hard substance) to 70° for vulcanised fibre (a soft compost). In general, the minerals have high critical temperatures, while in metals the C.T. ranges from 240° to 130°. As to the accuracy of these figures, they are

trustworthy to 5° in the case of glass and vitreous silica, which have received special attention. For the other materials, the figures are probably reliable only to 10° or 15° . There is some doubt about the case of tin. It melts at 230° , and when raised to 210° it certainly took the place shown in column 4, but as at that temperature the surface was yellow with oxide, this particular result must be considered doubtful.

Column 5 has only six entries. Many more have been observed, but as they are not quite consistent, they are omitted. Suppose a sheet of cork or ebonite be pressed and rubbed by an ordinary "flat-iron" when at a temperature, say, about 150° , it will descend in position as shown in the Table. Another method is, after warming a sheet, to place it between two sheets of its own material, and press the whole together while the hot sheet is pulled from between the others. This is called the Pressed-Hot (P.H.) state. It can be removed, in the case of hard bodies, such as glass, by passing the surface dexterously through the flame for a short time. If the surface be heated too long, it will go further and become abnormal.

Columns 6 and 7 should be considered together. In experiments to be described later (p. 26), it is shown that, under certain conditions of stress, a convex surface and a concave surface, both of one material, become charged in opposite senses. It will be seen that mica behaves in one way; paper, ebonite, and celluloid in the contrary way.

Thus the Table (p. 32) shows how readily the surfaces of a great variety of materials change their places in the series. A scrutiny will reveal that these changes occur according to very simple laws. Divide the second column in two groups, A, B, by drawing a demarcation line below place 14. Then it is observed that materials in Group A all move one way; those in Group B all move the contrary way. The laws of these movements may be tabulated thus:—

	Matt.	Abnormal.	P.H.	Convex.	Concave.
Group A	Down	Down	Up	Down	Up.
Group B	Up	Up	Down	Up	Down.

Another peculiarity in this grouping is that all the animal materials occur in Group A; all the vegetable materials in Group B.

The many empty spaces occurring in columns 3-7 are not blank through inadvertence. Practically all the suitable materials have been tested for these effects, but it has not been possible to perceive effects for all the diverse substances in the Table. In no case has any distinct result been

suppressed. But there have been a few cases where effects have been detected, but have been subsequently ignored, as they would not repeat. Thus glass, silica, and quartz have sometimes been obtained P.H. at place 2—but this effect is not consistent. The contrary influences found in the two groups I call *duality*.

Notes on the Behaviour of Mercury.

Before concluding the description of the Table (p. 32), mention should be made of the anomalous behaviour of mercury. It will be seen that this metal is placed with platinum and gold (place 34), and also high up (place 2). The effects observed are as follows:—

(1) When rods of various materials are gently pushed into mercury, every one in the series, except celluloid and indiarubber, will become charged +. Thus we assign to mercury place 34. If, however, the rods be plunged quickly into the mercury or stirred in it, they all, except asbestos, become —. Let us denote mercury when the friction is violent as (mercury'). Its place is 2. Possibly violence causes the rods to become extremely abnormal in contact with mercury. Lenard's theory (9) regarding "waterfall" electricity may be recalled. In the case of water, he supposes there is an electrified double layer, the external one being — and the internal +. If there be a similar double layer in mercury, the external one would be + and the internal —.

(2) Abnormal glass, polished or matt, is — to mercury even when immersed in it gently. Yet the same specimens of glass are + to gutta-percha, which itself is + to mercury. The same effect will be found for abnormal mica and other materials. Supposing the charges obtained when bodies are plunged into mercury are really due to friction, then the effect just recorded seems to mean that the abnormal surfaces are in reality below place 34, for such gentle friction as mercury provides, but that rubbing with solid surfaces so flattens, or otherwise affects, the surface particles as to bring the abnormal surface up, in the case of glass, to place 26.

(3) A glass rod plunged into mercury becomes highly charged. On repeating the process several times, however, the + charge becomes very small. But the original excitability is restored by rubbing the glass by hand or by a cotton duster. It is possible that the glass is rendered abnormal by mercury, and made normal again by rubbing.

(4) If mercury be raised in temperature, its power of exciting charges on solids immersed in it gradually lessens as temperature rises, returning again entirely at normal temperature. Thus, at 110°, the charge produced on ebonite is small, whether immersion be gentle or violent. Glass in mercury at the above temperature receives no charge for gentle immersion, but

receives a large charge when immersion is violent. When the mercury is at 200° , it will give no charge to any body under any conditions tried.

Notes of the Peculiar Behaviour of some Flexible Sheets.

(1) Take two strips, cut from the same sheet of transparent, polished celluloid. Place one sheet on the other, and draw them between thumb and first finger, bending the strips as they pass between the fingers. Now place the strips, still in contact, for a second in the discharge zone of a flame to remove the $-$ charges on their outer surfaces due to friction of the material on the fingers. On separating the strips, that one of the surfaces in contact which was convex when flexed is $+$, the other surface in contact, the concave one, being $-$. An effect of this sort was pointed out by Jamieson (7). Hence opposite charges arise from complex strains on the opposed surfaces. There is no special significance in using the fingers, identical effects being found if the fingers are replaced by other rubbers, say pieces of wood.

The above effects are recorded in the Table (p. 32), columns 6 and 7.

(2) Similar effects are found for two sheets of ebonite or cork, of filter paper or mica. But it is of interest to notice that mica, which is in Group A, acts in one way, whereas the other materials, which are in Group B, behave in the contrary way for convex and concave surfaces respectively.

(3) A variant of the above experiment is curious. Place the two celluloid strips in contact, and draw them between the fingers as before, but in this case leave them unflexed in the process. After removing the external $-$ charges as before in the discharge zone, the strips will be found to cling together strongly, and, when tested, are found to be charged, one $+$, the other $-$. This, of course, is a simpler experiment than (2), for now the two strips are treated identically throughout. The two surfaces in contact must differ in composition or condition, so as to act on one another, in effect, as different materials. It is a commonplace in tribo-electricity to find two surfaces apparently identical which, when rubbed together, excite one another with opposite charges. The present effect seems to be merely an example of this kind.

In experiment (1) the convex surface becomes always $+$ to the concave, however the surface of the two strips be changed about. But in experiment (3) the effect is peculiar, not to the material, but to a given specimen: if the surface is $+$ in one position, it will be $+$ always, whatever its position relative to the other surface. Thus, the effect in (1) depends on flexure, whereas in (3) it is simply characteristic of the materials used.

V.—*Theory*.

On the simple electronic theory of tribo-electric phenomena there are free electrons close to the surface of solids which readily leave the surface when rubbed. The materials high up in the series are supposed to be characterised by having electrons specially free to leave. This theory, as it stands, does not account for the presence in the Table, mixed in among insulating bodies which are poor in free electrons, of metals and alloys, all peculiar for their richness in free electrons. Nor is it evident how it can explain the effects in columns 3–7 in the Table. These are striking and consistent enough to call for an explanation. A theory is wanted. Moreover, a definite concept of surface conditions is needed for continued successful investigation of the subject.

The outstanding results are: (1) the order (not unmethodical) in which materials arrange themselves in column 2; (2) the duality found in columns 3–7 in the behaviour of the top and bottom sections of the series; (3) the principle of the critical temperature.

In commencing an enquiry into the basis of these effects the question arises as to any possible relation of chemical composition of the material to its position in the series. In the following list is given the composition of the materials used. They are arranged roughly in the order of column 2, except in those cases where like bodies are grouped together.

Material.	Composition.
GROUP A.	
Asbestos	Magnesium silicate.
Furs	
Wool	
Silk	
Felt	
Hand.	
Silica	
Glass	
Quartz	
Mica	K, Al, SiO ₂ .
Calcite	CaCO ₃ .
Borax	Na ₂ B ₄ O ₇ ·10H ₂ O.
Fluor spar	CaF ₂ .
Pb, Al, Zn, Cd, Mn, Cr.	
GROUP B.	
Vulcanised fibre	?
Filter paper	
Cotton	
Woods	
Cork	
Magnumium	(70 Al, 30 Mg).

Material.	Composition.
GROUP B—(contd.).	
Paraffin wax	Hydrocarbons, e.g. $C_{30}H_{62}$.
Potassium bichromate	$K_2Cr_2O_7$.
Amber	
Shellac	
Sealing wax	
Resin	
Potash alum	Mixtures of compounds of C, H, O, of unknown formula. Sealing wax sometimes has mineral matter in traces.
Chrome alum	
Iron alum	
Slate	
Ebonite	$KAl(SO_4)_2 \cdot 12 H_2O$.
Indiarubber	$KCr(SO_4)_2 \cdot 12 H_2O$.
Gutta-percha	$NH_4Fe(SO_4)_2 \cdot 12 H_2O$.
Iron pyrites	Aluminium silicate (hydrated).
Galena	
C.	
Cu, Sn, Sb, Co, Ni, Bi, Pd, Ag, As, Te, Pt, Hg, Au	
Celluloid	Hydrocarbons and sulphur.
	Similar to indiarubber, but without sulphur.
	FeS_2 .
	PbS .
	Nitro-cellulose (C, H, N, O) and camphor.

It is easy to detect characteristics special to each group.

Group A contains :—

- (1) Silicates, including the glass family, asbestos and mica.
- (2) All the animal materials.
- (3) The notably + metals and lead.

Group B contains :—

- (1) No silica compounds, but a great variety of carbon compounds.
- (2) All the vegetable materials.
- (3) Many metals, including those notably —.

There is no apparent gradation in density, but the hard silica compounds in Group A are in striking contrast to the soft bodies, especially the waxes, in Group B. Hydrated bodies are found in the lower rather than the upper group. The three alums are seen to be widely separated from one another in the order we should anticipate from the electro-potentials of their distinguishing metals.

Peculiar interest attaches to the elements, metallic (20 in number) and non-metallic (3 in number), in the series. Of the metals, all but two, lead and mercury, are arranged according to the electro-potential series of Ostwald (7A). Allowance must be made for the fact that owing to their conductivity metals rubbed together show no charges detectable by the present means; hence the metals are grouped in many cases as shown, no less than nine occurring at place 29. Mercury with electro-potential -1.03 is so

nearly the same as silver (-1.05) and palladium (-1.07) that its displacement in the series relative to these two metals may be ignored. This leaves lead as the only exception to the electro-potential order. Lead is undoubtedly peculiar, for with potential -0.13 it is above, for instance, aluminium with potential $+1.00$. Three distinct specimens of commercially pure lead behaved alike; and no change in behaviour was found after the metal had been melted and when cool cleaned on the surface. Commercial sheet lead is so pure that it is not considered necessary to try a specimen of special purity. An independent reason for supposing lead to be in Group A is that when abnormal it descends in the series to about the position of undoubted Group A metals, *e.g.* aluminium and zinc.

Apart from the metals, only three elementary solids, carbon, sulphur, and tellurium, have been tried. These highly negative elements occur, as we should expect, near the bottom of the series. One supposes that the other non-metallic elements, if obtainable in suitable solid form, would also take their place at or beyond the bottom of the list, and that the most strongly electro-positive elements, potassium and sodium, would occur high up in the series. In general the basogenic elements come above those with oxygenic qualities; yet the property of forming very stable oxides, sulphides, etc., would seem to be a better criterion of tribo-electric position than base- or acid-forming power. Thus if calcium or manganese be rubbed with their natural oxide on the surface they will take places far down in Group B; if cleaned, and the pure metal exposed, they are found in Group A. Again, silica is a prominent compound at the top of the series, whereas the inert metals, platinum and gold, are at the bottom. Now, if acid-forming power were considered, silicon should be low in the series and silica also very low, certainly not far above platinum and gold. These matters appear to be vitally important from the theoretical standpoint.

As to the critical temperature, the change from the normal to the abnormal state appears to be sudden. A rise of 10° or so suffices to take the surface from one state to the other. But glass at 220° (*i.e.* 23° below C.T.) has been found at place 20 in the series, as if it were in a transition state from normal to abnormal. In the cases of some metals, *e.g.*, silver and copper, the abnormal state has been looked for, but not detected. It is clear that in most metals it would be hopeless to look for a critical temperature higher than, say 300° , as oxide would then form readily on the surface. Closer and more extensive research may reveal the significance of these critical temperatures.

In scrutinising the series, one can detect nothing in the ordinary physical or chemical characteristics to elucidate the phenomenon of duality mentioned on p. 25.

The conditions at the actual surface of a solid are, of course, peculiar. The particles there are more free than below the surface. They are, in general, unprotected and, so to speak, raw and liable to strain, orientation, and disintegration by outside influences such as the impact of other solids. Tribo-electric charges are derived from the actual surface ; but whether from constituent parts of the atom or from interatomic or intermolecular sources is not decided. The theory will be very complicated if, as is possible, the charges are derived from two or more of these sources. The atom is the simplest unit, and would appear to be the most likely source, but the question must be left open at present.

Now, if two groups (*e.g.*, Groups A and B in the Table) of bodies behave in ways exactly contrary to one another, one might imagine each group to be characterised by its own kind of unit (whether atomic or molecular).

Suppose the characteristic of Group A is an α unit, that of Group B a β unit. If we assign certain qualities to the units, then in any surface the units would decide how the surface would change its place in the series when its condition is changed. According as the α or β units predominate in the material the action will be that of Group A or Group B in the Table on p. 32. The case has been stated here in the most general way. It would be premature to go further and outline the model which I have had in mind throughout the experiments, and which has successfully indicated the course to pursue in these investigations.

Something should be said about the principle of the electric double layer by which many physicists, *e.g.* J. J. Thomson (8) and P. Lenard (9), have interpreted surface effects. Amongst others, O. W. Richardson (10) has explained the fact that in thermionic experiments a definite amount of work must be spent to enable an electron to escape from a heated solid surface. The view is generally held that the $-$ layer is always outermost of the two layers. Again, R. A. Millikan (11) has given new support to the principle by proving the exactness of Einstein's formula $\frac{1}{2}mv^2 = h(\nu - \nu_0)$ for photo-electric effects on certain metals.

Recently, J. Frenkel (12) has developed the idea. Assuming that all positions and all orientations of an atom at the surface are equally probable, he explains the double-layer principle on the simplest basis. For if Rutherford's nuclear atoms be placed in all positions and all orientations at the surface, the electron orbits will in the aggregate project beyond the $+$ nuclei, and there will be established a $-$ layer outside a $+$ layer.

Frenkel carries on the argument, successfully applying the principle to a great variety of surface effects. In short, the evidence in favour of the double-layer effect seems overwhelming.

However, the results of the present paper may be taken to show that whereas all orientations at the surface are equally probable for the abnormal state, and less so for the matt state, yet for the normal and pressed states the surface particles are orientated unequally ; a quasi-mechanical strain being imposed (by rubbing) on the surface particles.

As an analogy, imagine a row of pivoted magnetic needles all pointing N., but their centres in line E. and W. If the pole of a bar magnet be taken along the line near but not touching the needles, these will, if at suitable distances from one another, be left at the end of the operation pointing in line E. and W. The bar magnet has orientated them, and they are left in a stable condition of strain. Jolting the system would cause a release from the strained state of the needles, just as heat causes the release from the normal to the abnormal state in the case of the tribo-electric experiments.

Orientation of surface atoms would be tantamount to bringing the outer — layer and the inner + layer nearer to one another.

Another type of atom, though not apparently one of the Rutherford pattern, might produce at the surface of a solid a double layer with the + layer outermost. If this were so, we could explain the effects of Group A, by imagining the new type of atom predominant in those materials ; and the effects of Group B by having the Rutherford atom predominant in the materials of this group.

Whether, in the double layer, the — layer or the + layer be outermost at the surface, the layers would be most separated from one another in the abnormal state and least separated in the pressed state.

VI.—Conclusion.

The endeavour is made to direct attention to a long-neglected field of research. The results revealed are considered sufficiently novel for publication as they stand. With more refined experimental methods the subject will advance no doubt from its present stage ; but the process will be slow. Quantitative work on materials *in vacuo* cannot easily be done when, as here, considerable mechanical force has often to be applied to the materials. But this is not the only reason for expecting slow progress. The materials possible to be tested are unlimited, and generalisations should not be based on a few instances only.

In the last few years the surface conditions of solids have been investigated from new standpoints. To mention two instances bearing on our experiments : H. L. Curtis (13) has observed enormous change (as much as one hundred million-fold) in the surface conductivity of insulators as the relative humidity of the air over the surfaces varies from 20 to 90 per cent.

This brings in the moot subject of adsorption, which one would expect to have a bearing on tribo-electric effects. Mr. C. Hayes and I have observed a direct connection between dampness of a surface and the sign of the charges it gives when rubbed. Again, J. W. French (14) has discovered that the surface of artificially polished glass to a depth of $5\ \mu$ is of a peculiar nature, differing in cohesion from the main underlying material. Mr. Hayes and I have found that the surface of polished glass has under some conditions a neutral state. In this state it yields neither + nor - charges. This effect is found only in the artificially polished material.

Any theory on this subject to be acceptable should embrace not only the effects included in the Table, p. 32, but also several others such as the varied results obtained (see p. 22) according as one surface is brushed, rubbed, or struck by another. The theory should take cognisance, also, of the peculiar behaviour of mercury (p. 25), though as mercury is the only liquid used in these experiments its case is singular.

This paper is meant to be the first of a succession on the subject of tribo-electricity. Some quantitative work has already been done on various branches of the subject, *e.g.*, the influence on the surfaces about to be rubbed of (1) low vacua; (2) electric high-potential discharge; (3) various liquids. Mr. C. Hayes, M.Sc., has worked with me for a considerable time on these subjects. I am glad to acknowledge valuable help in obtaining data for the present paper from him and from Miss H. M. Browning, B.Sc. I also wish to acknowledge my indebtedness to Prof. G. A. Schott, D.Sc., for valued advice as to theory.

VII.—*Summary.*

(1) The tribo-electric series, in which solid materials are arranged in order according to the charge they acquire when rubbed together, is reliable with due precautions. In the Table are shown the common solid metallic and non-metallic elements, interspersed with a great variety of compound materials.

(2) Most solids are found to alter their place in the series if heated above a certain temperature, which is specific for each material. This temperature is called the critical temperature. The surface in its new condition is termed abnormal.

(3) The series may be divided into an upper Group A and a lower Group B. It is found that these groups have tendencies contrary to one another as the surfaces of the materials are rendered (*a*) matt, or (*b*) abnormal, or (*c*) pressed, or (*d*) flexed. If under any of these agencies Group A becomes more + forming, Group B becomes more - forming, and *vice versa*. This principle is here called duality. It is possible that the

Dr. P. E. Shaw.

Table showing the Tribo-electric Normal Series, Column 2, with Variations for Matt, Abnormal, Pressed respectively. The more important materials are in capitals. Metals

GROUP A.

Place.	Materials in normal series.	Prepared matt surfaces.	Abnormal (and critical temperature in ° C.).	P.H. (p. 24).	Flexed.		Place.	Materials in normal series.
					Convex.	Concave.		
1	ASBESTOS (sheet). +						15	FILTER PAPER.
2	RABBIT'S FUR, Hair (Hg').						16	VULCANISED FIBRE
3	GLASS (Combn.-Tube).						17	COTTON
4	VITREOUS SILICA, OPOS- SUM'S FUR.						18	Magnalium
5	GLASS (fusn.)			Mica		Mica.	19	Potash alum, rock salt, satin spar
6	MICA.						20	Woods, Fe
7	WOOL				Mica.		21	Unglazed porcelain, sal-ammoniac
8	GLASS (pol.), QUARTZ (pol.), glazed porcelain.						22	Potassium bichromate, PARAFFIN, tinned iron.
9	GLASS (brn.-edge), ivory.						23	CORK, ebony
10	CALCITE			Wool	Zn.		24	Amber
11	CAT'S FUR.						25	Slate, chrome alum
12	Ca, Mg, Pb, fluor spar, borax.						26	SHELLAC, RESIN, SEAL- ING WAX
13	SILK.						27	
14	Al, Mn, Zn, Cd, Cr, FELT, hand, wash leather	CALCITE	Silk. Cd (200)		F. paper.		28	EBONITE
							29	Co, Ni, Sn, Cu, As, Bi, Sb, Ag, Pd, Carbon, Te, eureka straw, copper sulphate, brass
							30	PARA RUBBER, iron alum
							31	GUTTA-PERCHA
							32	
							33	SULPHUR.
							34	Pt, Hg, Au
							35	CELLULOID.
							36	INDIARUBBER
								—

V.
M.
W.
V.
Q.
G.
Co

SE
RE
SH

EF

CE
SU

[To face p. 32.

Pressed and Flexed States in Columns 3, 4, 5, 6, and 7
Metals are italics.

GROUP B.

mat	Prepared matt surfaces.	Abnormal (and critical temperature in ° C.).	P.H. (p. 24).	Flexed.	
				Convex.	Concave.
3 : salt, n, sal- mate, l iron.	V. fibre	Ca (240)? Calcite(270).			F. paper.
	MICA				
	WOODS,				
	V. SILICA				
	Quartz				
	GLASS				
	COMBN. TUBE	V. fibre (70) Ebonite(100) Pb (240).	F. paper. Woods.		
	SEALING WAX.	Al (240) Zn (220). Fe (200).		Cork.	
	RESIN		Cork.		
	SHELLAC.			Cork.	
1 SEAL-		V. silica 245. Glass (245). Mica (270). Quartz(300). Brass.			
	EBONITE	Ni (200) Sb (180). Sn (210)?		Ebonite.	
			Ebonite.		Ebonite.
s, Bi, arbon, straw, brass alum		Celluloid. Au (130). Pt (130). Indiarubber.			
	CELLULOID SULPHUR		Celluloid		Celluloid.

phenomena observed by Héséhous with radium may be another case of this duality of action, for glass is in Group A and ebonite in Group B.

(4) Anomalous effects are observed when liquid mercury is used as one of the materials, its behaviour being quite unlike that of solid surfaces.

(5) As to theory, it is suggested that the prevalent idea that the electric double layer, existing at the surface of solids, has the — layer outermost in all cases is incorrect. Normally, the materials in Group A would have — outermost, those in Group B having + outermost. Orientation of surface atoms would give rise to changes in the disposition of the two electric layers, and so account for observed effects.

(6) Tribo-electricity undoubtedly affords a means of extraordinary delicacy, of discriminating between materials apparently alike.

LIST OF REFERENCES.

1. Chwolson, O. D., 'Traité de Physique,' vol. 4, Fasc. 1, pp. 264-9.
2. Wiedemann, G., 'Die Lehre von der Electricität,' pp. 208-220.
3. Héséhous, N. A., 'Jurn. Russk. Fisik-Chimicesk.,' Obsčestva 34, pp. 1-15 (1902); 35, pp. 575-80 (1903); 37, pp. 29-33 (1905).
4. Morris-Owen, 'Phil. Mag.,' April, 1909.
5. Morris-Jones, W., 'Phil. Mag.,' February, 1915.
6. Shaw, P. E., 'Proc. Phys. Soc.,' vol. 27, April, 1915.
7. Jamieson, W., 'Nature,' vol. 83, p. 189, April 14 (1910).
- 7A. Ostwald, W., 'Lehrbuch der allgemeinen Chemie,' vol. 2; also 'General Inorganic Chemistry,' by Alexr. Smith (Geo. Bell), p. 670.
8. Thomson, J. J., 'Camb. Phil. Soc. Proc.,' vol. 14, p. 105 (March, 1907).
9. Lenard, P., 'Ann. d. Physik,' vol. 47, 4, pp. 463-524 (July 8, 1915).
10. Richardson, O. W., 'Emission of Electricity from Hot Bodies.'
11. Millikan, R. A., 'Phys. Rev.,' vol. 6, p. 55 (July, 1915).
12. Frenkel, J., 'Phil. Mag.,' April, 1917.
13. Curtis, H. L., 'Scientific Papers, Bureau of Standards (U.S.A.),' No. 234, June, 1914.
14. French, J. W., 'Trans. Optical Soc.,' November, 1916, and February, 1917.

Table showing the Total cluster Reward Score, Column 1, and Total Score for Best observed, Forecast and Worst Score in Columns 2-4, 5-6 and 7, respectively. Scores for worst individuals are in brackets. Scores are italicized.

10

10 of 10